



Electrochemical Capacities of Commercially Available Structural Carbon Fibers, Fabrics, and Papers

by Emma L. Wong, James F. Snyder, and Clifford W. Hubbard

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Weapons and Materials Research Directorate, ARL

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Summary

This study focuses on the energy storage properties of commercial carbon fabric materials. Electrochemically active carbon fabrics could facilitate scalable development of multifunctional fiber-based structural composites or fabric-based wearable components that provide a secondary function as a battery or supercapacitor. Multifunctional composites are desirable to reduce system mass by integrating load-bearing and energy storage capabilities into a single material. Electrochemical capacity and double layer capacitance were evaluated for a wide range of structural carbon fibers based on poly(acrylonitrile) (PAN), pitch, or activated carbon; and papers made from carbon nanotubes or nanofoams. The impact of fiber sizing on electrochemical activity was also studied. The data is tabulated with manufacturer-reported material properties to enable rapid identification of fibers or fabrics for a wide range of potential applications. PAN-based fibers and nanofoam papers demonstrated reversible capacities as high as 186 mA·h/g. Fiber sizing did not appear to be a detriment to electrochemical activity. The T-300 PAN-based fibers are most recommended for use in multifunctional composite batteries given their high tensile strength and high capacities. Double layer capacitances for activated carbon fibers, nanotube fibers, and nanofoam papers consistently approached or exceeded 10 F/g.

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1. Introduction

The need for energy storage devices with higher energy densities, lower weight and volume, and more efficient form factors has driven research into a wide variety of new electrode materials (1–4). Carbon is a commonly used material for anodes in modern technologies, particularly in lithium-ion batteries and electrochemical supercapacitors. Graphitic carbon allows for efficient ion intercalation and is of particular interest for the former (5, 6), while carbon with a high surface area optimizes use of the double layer effect and is desirable for the latter (4, 7).

Considerable effort has been directed towards surpassing graphite's theoretical capacity of 372 mA·h/g using non-carbonaceous materials such as metal oxides and tin alloys (1, 3, 8). Other groups have focused on improving the electrochemical properties of alternative forms of carbon such as carbon fibers (2, 8, 11), carbon nanotubes (1, 14, 17), and carbon foams (4, 18, 19). These carbon-based materials are particularly attractive owing to their continuous structure and inherent electrical conductivity, obviating the need for a polymer binder and metal substrate that add parasitic mass in granular carbon anodes. Carbon fibers have also been shown to perform well in overcharge as a result of minimized heat-generating side reactions and excess lithium ion capacity (20–22).

The properties of carbonaceous materials are dependent on the processing conditions and source material that largely determine the composition and structure of the material. Carbon fibers typically have an amorphous core surrounded by a graphitic sheath that allows for efficient ion intercalation. Poly(acrylonitrile) (PAN)-based fibers have moderate graphite content and under proper conditions provide superior failure strength, tensile strength, and compressive strength, making PAN-based fibers useful for structural composite applications (23). Pitch-based fibers when compared to PAN-based fibers are more graphitized, and have higher cost, density, thermal conductivity, and electrical conductivity (10, 23). Carbon nanofoams are a carbonized product of polymer aerogels combined with carbon fibers. They have demonstrated favorable anodic properties (4, 18, 19) and have been developed for commercial electrode use (24).

Non-graphitic fibers are also commercially available, such as fibers composed of activated carbon. These are comprised entirely of amorphous carbon and have a high surface area and good microporosity (7, 25). These materials are not typically considered without chemical modification (25) for use in batteries due to the low graphite content, although their high surface area makes them potentially attractive for high capacitance applications (7). Carbon nanotubes and nanofoams also possess high surface areas that are ideal for high capacitance applications (15). For battery applications, the concentric continuous graphitic cylinders comprising carbon nanotubes indicate additional capability for optimizing ion intercalation. While recent work indicates that the partially graphitized nature of PAN- and pitch-based fibers may be beneficial for anodic properties (9), using carbon nanotubes by themselves or as additives to other

intercalative materials has been shown to improve capacities beyond that of pure graphite, 372 mA*h/g (17). One study has reported an initial electrochemical capacity as high as 1770 mA*h/g from a combination of multi-walled nanotubes with silicon (16).

Previous studies on structural carbon, including fibers, nanotubes, and nanofoams, have focused their efforts on improving the electrochemical properties prior to testing through heat treatment (9–12), milling (9–12, 16, 17), chemical modification (1, 9), and/or additives such as carbon black (11) and metals (26). Some of these techniques have elicited materials with capacities superior to that of pure graphite (16). In many cases these modifications eradicated or significantly reduced the structural properties the carbon sources originally had. There is also little indication of the impact on electrochemical properties from fiber sizing or binders, which are removed or reduced during modification. In addition, the tested materials were individually processed or fabricated and are not commercially available. The electrochemical performance of commercial off-the-shelf (COTS) structural carbon materials has not been adequately reported. An evaluation of the properties of unmodified COTS materials would indicate their usefulness in electrochemical devices and would provide a baseline for comparison with the specialized lab-grown or modified materials reported elsewhere. There is particular interest in COTS structural carbon materials for use in multifunctional composite devices, such as structural batteries (27–32).

In this study, we investigated the performance of unmodified COTS carbon materials for potential anode applications. Particular focus is currently placed on electrochemical capacity, and some preliminary capacitance data are also reported. A broad variety of structural carbon sources were surveyed, including carbon fibers acquired from fabrics of varying composition, manufacture, and grade; carbon nanotubes; and carbon nanofoams. Several fiber types were also desized to demonstrate the impact of sizing or binding on the electrochemical properties. Downselected materials demonstrating useful capacity or capacitance will be reported in greater depth in a future publication detailing the explicit electrochemical-mechanical properties of carbon reinforced multifunctional composites.

2. Experimental Section

2.1 Materials

Table 1 lists the samples procured for this study. PAN- and pitch-based fibers were tested in both commercial grade and aerospace grade. Commercial grade is made from larger tows and then pulled apart to make smaller tows. This process makes the fibers more frayed and less smooth, and generates more inclusions and flaws. The aerospace grade fibers are made in smaller tows and the fibers have cleaner tow/surface morphology (23). Each grade has possible advantages for anodic activity. Commercial grade fibers are rougher on the surface, which may give the fiber

more active surface area. On the other hand, the aerospace grade, being more morphologically uniform, can retain a better graphitic structure and a larger number of sites for lithium intercalation.

Table 1. Manufacturer-provided and the U.S. Army Research Laboratory (ARL)-measured data of commercial carbon fibers and fabrics.

Grade	Fiber Density (g/cm ³)	Fiber Length	Fiber Diameter (microns)	Sizing/Binder (%)	Fiber Tensile Strength (MPa)	Resistance (Ohm/mm)	Resistivity (Ohm-mm)	Capacitance (F/g)	Capacity (mAh/g)
<u>Granular Carbon Film, 80 wt%</u>									
Graphite							0.06		74
Activated Carbon							153		3
Lamp Black							<1		89
<u>Pitch-Based Fibers – Woven Fabrics</u>									
YSH70A	2.14	continuous	7	1.60%	3811	0.077		0.4	32
YSH50A	2.1	continuous	7	1.90%	3687	0.074		0.38	40
YS80A	2.17	continuous	7	1.60%	3626	0.068		0.8	18
YS95A	2.2	continuous	7	2.10%	3745	0.070		1.1	23
CN90	2.19	continuous	10	2.70%	3419	0.051		0.68	14
CN60	2.12	continuous	10	2.90%	3331	0.055		0.81	76
XN15	1.85	continuous	10	3%	2378	0.35		0.42	52
XN05	1.7	continuous	10	2.60%	1157	0.23		0.5	45
K-1100	2.2	continuous	10	1%	3100	0.050	0.001	0.87	32
<u>PAN-Based Fibers – Woven Fabrics</u>									
AS4	1.79	continuous	7.1	1%	4278	2.4	0.60	1.3	88
IM7, 6k	1.79	continuous	5.2	1%	5175	1.3	0.26	3.2	131
IM7, 12k	1.79	continuous	5.1	1%	5605		0.61	0.92	67
PANEX 30	1.75	continuous	7.4	---	3600		0.22	0.0017	70
PANEX 35	1.81	continuous	7.2	4.20%	3860		0.38		128
T-300, 1k	1.76	continuous	7	1%	3530	2.9	0.11	1	139
T-300, 3k	1.76	continuous	7	1%	3530	3.7	0.52		166
T40/800	1.79	continuous	5.1	AP-200	5520	0.84	0.16	3.5	74
<u>PAN-Based Fibers – Nonwoven Mats</u>									
8000015		25 mm		1%			0.85		89
8000020		25 mm		1%			0.64		48
8000028		13 mm		1%			0.63		55
8000030		25 mm		1%			0.49	1.1	96
8000033		25 mm		1%			0.64		94
8000036		13 mm		1%			1.05	1.88	106
8000037		13 mm		1%			0.74	1	78
8000039		6.4 mm		1%			0.95		107
8000047		6.4mm and 25mm		1%			1.48		114
1064		continuous (>51mm)					0.44	6.7	99
<u>Activated Carbon Fibers – Woven Fabric</u>									
2225		continuous					8.97	7.4	102
<u>Activated Carbon Fibers – Nonwoven Mats</u>									
14/86							364	15.6	64
<u>Nanotube Paper</u>									
SWNT		1-10 μ m	0.001-0.003	---			0.1	8.45	76
MWNT		5-20 μ m	0.03+/-0.015	---			0.1	12.5	89
BPNT		5-20 μ m	0.03+/-0.015	---			0.1	25	96
<u>Nanofoam Paper</u>									
I				---			0.28	7.19	149
II				---			0.48	5.68	136

2.1.1 PAN-based Fabrics/Fibers

PAN-based fibers were obtained from both woven and nonwoven carbon fabrics. Nonwoven fabrics come in two forms: chopped fiber mat and continuous fiber mat. The chopped mats were obtained from Hollingsworth and Vose in grades: 8000015, 8000020, 8000028, 8000030, 8000033, 8000036, 8000037, 8000039, and 8000047. The chopped mats have short uniform fiber lengths (6.4–25 mm) and can have more than one fiber length in the mat. The continuous fiber mat, product 1064 carbon fiber veil, was from Fibre Glast Developments Corporation. The continuous fiber mat has longer fiber lengths than the chopped fiber lengths (>51 mm). The PAN-based woven fabrics obtained for study came from multiple sources as unidirectional or plain woven and in variable tow sizes described as “nk”. The specific grades were T300 (plain 1k and plain 3k; Torayca), AS4 (Hexcel), IM7 (plain 6k and unidirectional 12k; Hexcel), PX30 (plain; Zoltek), PX35 (unidirectional; Zoltek), and T40/800 (plain 6k; Thornel). PX30 and PX35 are commercial grade fibers, and the rest are aerospace grade.

2.1.2 Pitch-based Fibers

Pitch-based carbon fibers were obtained from Nippon Graphite Fibers, with the exception of K1100, which was obtained from Cytec. Grades K1100, YSH70A, YSH50A, YS80A, and YS95A are aerospace grade graphitized fibers with an amorphous core. Grades CN90 and CN60 are commercial grade graphitized fibers with an amorphous core. Grades XN15 and XN05 are commercial grade fibers that are entirely amorphous.

2.1.3 Activated Carbon-based Fiber

Activated carbon fabrics were purchased from Engineered Fibers Tech. SpectraCarb 2225 is a woven fabric with a surface area of 1650 m²/g (25), and Sterling Fibers’ filtration media 14/86 (fibrillated acrylic fiber pulp (CFF)/activated carbon (AC)) is a nonwoven fabric.

2.1.4 Nanotubes

Carbon nanotube sheets were purchased from Nanolab in three varieties: single-wall nanotube (SWNT), multi-wall nanotube (MWNT), and bamboo multi-wall nanotube (BPNT).

2.1.5 Nanofoams

Carbon nanofoam sheets were procured from Marketech Inc. in grades I and II, which have respective surface areas of 400 m²/g and 600 m²/g.

2.2 De-sizing

To evaluate the impact of fiber sizing on electrochemical properties, the sizing was removed from select carbon fibers by solvent extraction using a Soxhlet extractor and methylene chloride for 48 h (33). The materials modified through this process included PX-30, PX-35, T40/800 6k, T300 1k, and IM7 6k. The IM7 12k was treated in a similar manner for seven days. The fibers

were then heated under vacuum for 10 min at 80 °C to drive off excess solvent. The treated fibers were imaged by a Field Emission Scanning Electron Microscope (FE-SEM) before and after solvent extraction to observe the extent of sizing removal. Heat treatment to burn off sizing was not employed as this has been shown to have a significant detrimental impact on fiber structural performance.

2.3 Electrochemical Analyses

Prior to measuring the electrochemical properties of the carbon materials, the fiber resistance or fabric resistivity of each material was measured with a multi-meter. The resistance of the fibers was normalized by the length of the samples, and the resistivity of the fabrics was normalized by the cross-sectional area and length of the sample.

Measurements of electrochemical properties were performed in a coin cell configuration requiring a 10 mm circular area of material. Nonwoven samples, including the sized and de-sized nonwoven fabrics, carbon nanotube paper, and carbon nanofoam paper, were cut into 10 mm disks. The sized and de-sized woven fabrics were unraveled and the fibers cut into 9 mm strands. The pitch-based fibers were also cut into 9 mm strands. Granular graphite was solvent cast from acetonitrile on stainless steel disks with 20 wt% poly(ethylene oxide) (PEO) 200k Da as a binder (2, 6). The carbonaceous materials were placed into coin cells with a lithium metal opposing electrode. The separators used were polypropylene separators from Celgard and Hollingsworth & Vose. A liquid electrolyte of ethylene carbonate: ethyl methyl carbonate (3:7 by weight) with 1.0 M lithium hexafluorophosphate (LiPF_6) was used.

Electrochemical capacity was measured on a Maccor 4000 battery test system at a constant current for 52 cycles. The cells were run at 9×10^{-5} Ampere between 0.002 V and 1.5 V over the first three cycles during formation of the solid electrolyte interface (SEI) layer (34). The remaining cycles were run at 3×10^{-4} A. The capacity values in table 1 were measured at the completion of the third cycle to approximate the reversible capacity. Capacity values were normalized by weight for comparison. The reported values are an average of at least three different experiments for each sample, with the exception of the lamp black and activated carbon powders, PAN IM7 6k, pitch YS95A, and BPNT, for which only one sample was successfully completed. The error, derived from standard deviations, was approximately 30% for PAN-based fibers, 50% for pitch- and activated carbon fibers, and 10% for nanotubes.

Capacitance was measured in the same coin cell configuration using cyclic voltammetry at a rate of 20 mV/s. The cells were cycled five times before taking the current measurement. Capacitance was determined from the ratio of current over rate and normalized by weight.

3. Results and Discussion

Table 1 reports the electrical and electrochemical properties measured for each of the samples along with several relevant material properties disclosed by the suppliers. The resistances and resistivities were sufficiently low enough such that all of the materials tested are expected to be able to perform adequately as current collectors and conductors for energy storage devices. The low resistances also enable reliable measurements of the electrochemical capacities and capacitances. Differences in the electrochemical properties for the materials studied may therefore be attributed primarily to changes in composition, dimensions, and interface.

Capacitance is a phenomenon that depends heavily on surface area. This is reflected in the significantly higher capacitance values for fabrics and papers made from high surface area materials, including nanotubes, nanofoams, and activated carbons. Most of the pitch-based fibers have capacitance values about an order of magnitude lower, generally less than 1 F/g. The PAN-based fibers exhibit a wide range of values but most of the values appear to be 1–3 F/g. Fiber dimensions are approximately the same for the latter and the outer shells of PAN fibers are typically graphitic, so the divergence in values between grades may reflect differences in sizing since the outliers have unique sizing applied. The discrepancy may also reflect differences in alignment of the graphite sheets in the shell as a product of processing. Similarly, the range of values between pitch-based materials may also relate to changes in the size and nature of the surface area as processing conditions are varied. Further work is needed measuring surface area and imaging the surfaces before more in-depth conclusions may be made. In general, the more structural PAN-based fibers are found to provide meaningful capacitance for low energy density applications, and higher efficiency devices could feasibly be made using activated carbon fibers, which are cheaper, more plentiful, and easier to process than nanotubes and nanofoams while providing competitive charge storage capability.

The electrochemical capacity data do not align so clearly with material source. This is because capacity involves ion intercalation, a complex process that depends not only on the interface and dimensions but also on composition. Intercalation in graphite has been studied for many years and graphite has been a predominant focus for anodic materials. Intercalation is not as well understood in other forms of carbon such as nanotubes, nanofoams, and even amorphous carbon; and materials with multiple phases interfacing each other present an even more complex challenge.

The nanofoams demonstrated the best overall performance as a material type. However, their tensile strength is approximately that of paper and they are not as practical for applications as the other types. Fibers incorporating aerogels, or more structural forms of aerogels, may be considered for future multifunctional material development. The other two nontraditional fiber

types, comprised of nanotubes and activated carbons, performed reasonably well. The capacity data for nanotubes follow an approximate trend mirroring that for capacitance, although further analyses should be performed to reduce statistical error and confirm these relationships.

With regard to more traditional structural fibers, those using PAN-based precursors significantly outperformed the pitch-based fibers. Surprisingly, all of the pitch-based materials also underperformed the baseline granular graphite film. Considering that pitch-based materials have higher graphitic content than PAN-based materials, the graphite layers may be more accessible in PAN-based fibers. It is also possible that the larger amorphous carbon cores in PAN-based fibers more efficiently augment the capability for ion uptake, which has also been suggested in previous studies (9). A third possibility is potential difficulty of the ions to reach the fiber itself due to the sizing. During processing, all of the fibers had any of a variety of proprietary sizings applied. Sizing composition, application, and quantity could all affect performance. Similar problems at the interface could potentially occur with binders in nonwoven fabrics. For this reason, several of the PAN-based fibers were de-sized using a literature preparation, and one fiber was de-sized for an extended period.

Table 2 presents electrochemical capacity data for sized and de-sized fibers, with each data point representing an average over three samples. Notable samples are IM7 12k, which was de-sized for significantly longer than recommended by the literature; PX-30, which is listed as having no sizing; and PX-35, which is listed as having considerably more sizing than the other fibers. While there is some variability in the results, it is clear that for sized fibers there is a capacity loss typically on the order of 30% after formation of the SEI layer and that the reversible capacity is generally stable over the first 52 cycles. De-sizing the fibers for 48 hours resulted in a reversible capacity that declines substantially with cycling for several sized samples. Although several desized samples showed apparent improvement over their unmodified counterparts, only the IM7 12k shows capacity of desized fibers to be equal to or improved over the unmodified fibers after 50 cycles. A possible explanation is that the sizing was not adequately removed at 48 h, but perhaps partially redistributed as a uniform layer on the fibers.

Figures 1–6 illustrate representative FE-SEM images of sized and de-sized materials. Nonwoven 8000036 was not tested electrochemically and did not appear in table 2. The dark gray matter on the sized fibers is the sizing. In some of the images it is evident that the sizing was removed, although it is possible that it was redistributed in a layer on the fibers so thin or transparent that it cannot be resolved in the FE-SEM images. In this scenario, the sizing may be interfering with formation of the SEI layer and possibly creating a more widespread barrier for ion migration. De-sizing may actually hurt performance if not performed adequately, and if it is performed adequately it appears to have little impact on performance in comparison to the sized material.

It should be noted that these studies were performed using a liquid electrolyte that may be effectively penetrating the sizing. The effectiveness of this technique, and/or the need for it, may be different for the pitch-based fibers, as well as cells using solid or polymer electrolytes, and

further studies are underway. However, for the purposes of the current study, the removal of sizing from COTS PAN-based fibers was not found to be justified. This conclusion is especially true for application in composites in which the sizing is important for establishing fiber-matrix bonding and removal of the sizing can diminish structural performance.

Table 2. Capacity measurements for sized and de-sized commercial carbon fibers.

Grade	Capacity (mAh/g)					
	1st cycle	Sized 3rd cycle	52nd cycle	1st cycle	3rd cycle	52nd cycle
IM7 6k	198	131	146	169	75	26
IM7 12k	127	67	57	167	77	76
PX-30	96	70	78	99	69	50
PX-35	182	128	118	141	82	75
T-300 1k	222	139	124	52	31	17
T40/800 6k	109	74	80	182	103	64

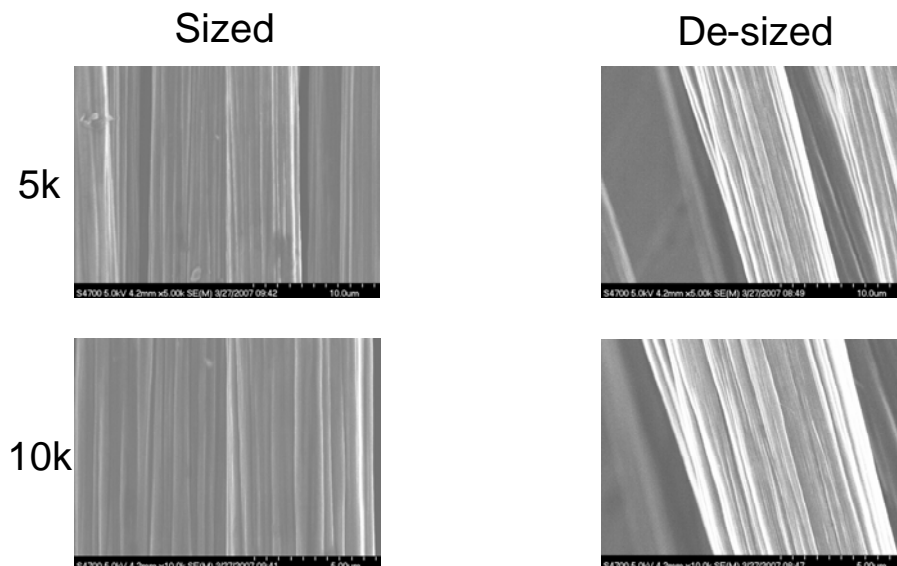


Figure 1. FE-SEM images of T300-1K tow fibers at 5 keV with 5,000 \times and 10,000 \times magnification. Commercial sized fibers that are unmodified (left) and de-sized at ARL (right) are both shown. The fibers were taken from a plain weave fabric.

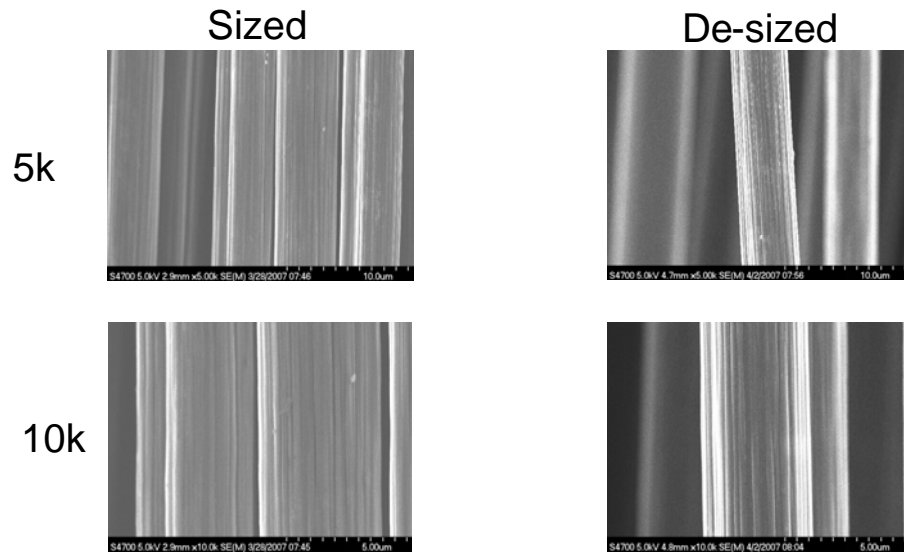


Figure 2. FE-SEM images of T40/800-6K tow fibers at 5 keV with 5,000 \times and 10,000 \times magnification. Commercial sized fibers that are unmodified (left) and de-sized at ARL (right) are both shown. The fibers were taken from a plain weave fabric.

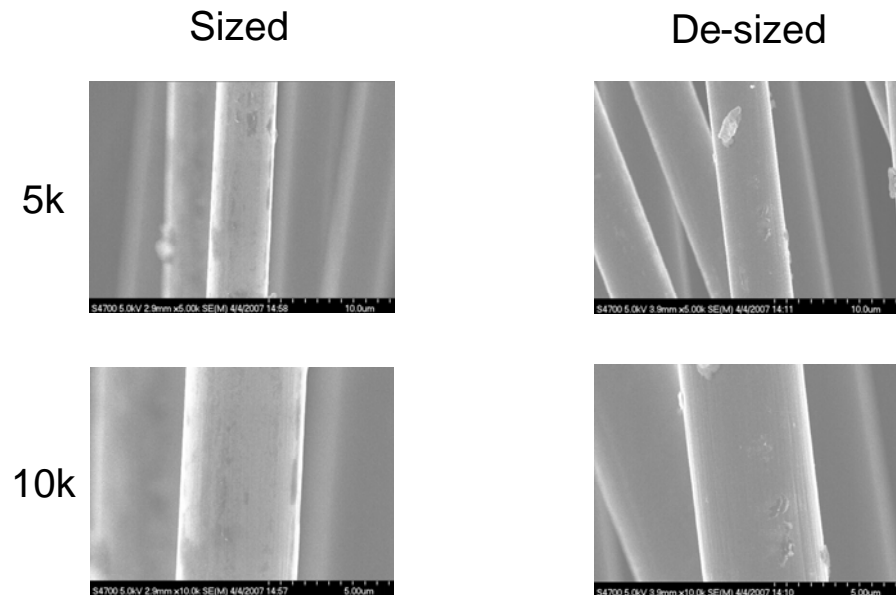


Figure 3. FE-SEM images of IM7-6K tow fibers at 5 keV with 5,000 \times and 10,000 \times magnification. Commercial sized fibers that are unmodified (left) and de-sized at ARL (right) are both shown. The fibers were taken from a plain weave fabric.

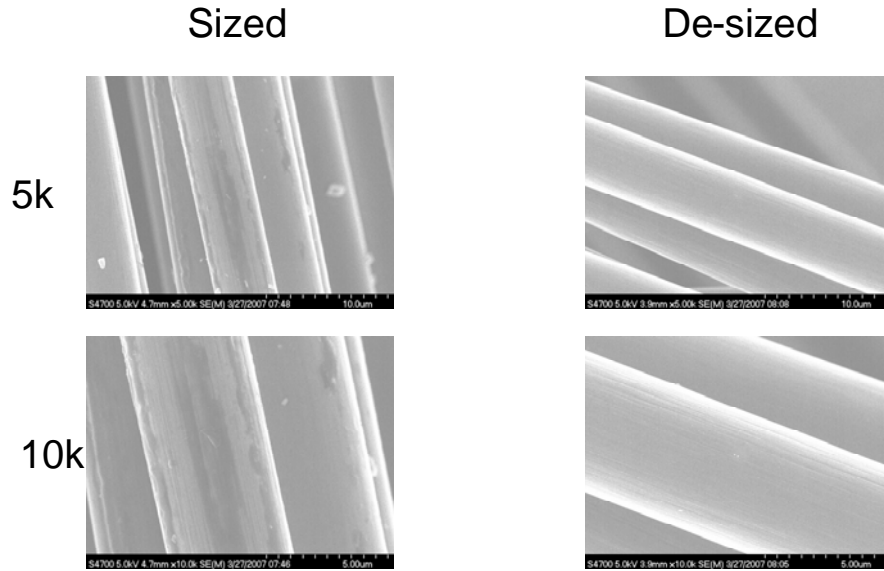


Figure 4. FE-SEM images of IM7-12K tow fibers at 5 keV with 5,000 \times and 10,000 \times magnification. Commercial sized fibers that are unmodified (left) and de-sized at ARL (right) are both shown. The fibers were taken from a unidirectional fabric.

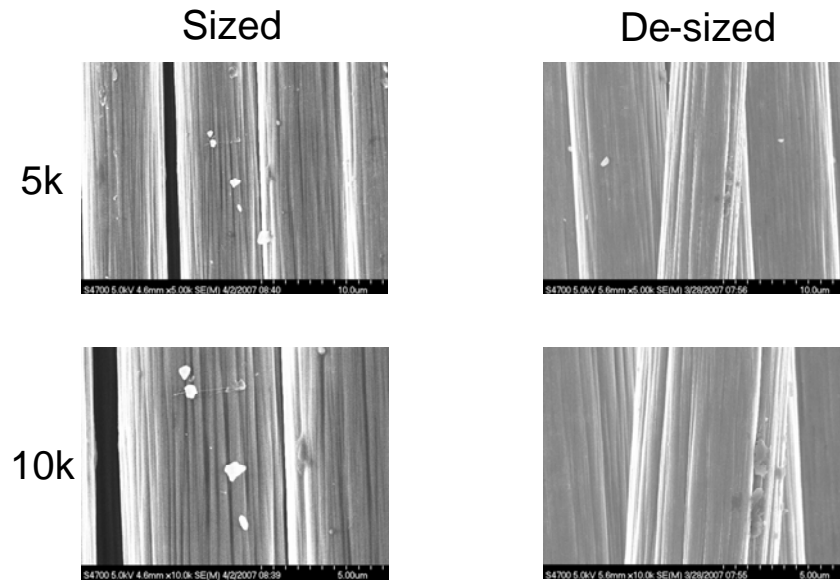


Figure 5. FE-SEM images of PX35-50K tow fibers at 5 keV with 5,000 \times and 10,000 \times magnification. Commercial sized fibers that are unmodified (left) and de-sized at ARL (right) are both shown. The fibers were taken from a unidirectional fabric.

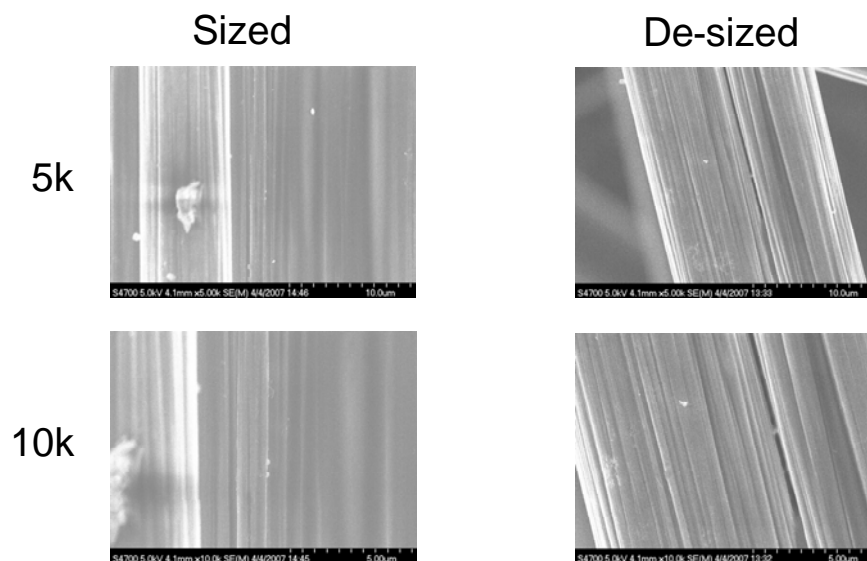


Figure 6. FE-SEM images of fibers removed from a H&V 8000036 nonwoven fabric. The images are at 5 keV with 5,000 \times and 10,000 \times magnification. Commercial fibers that are unmodified (left) and with binder removed at ARL (right) are both shown.

Fiber dimensions also appear to impact electrochemical capacity. This is particularly evident with the nonwoven PAN-based carbon fiber mats, which all use the same type of fiber. The nonwoven binder is anticipated to have minimal impact on comparative performance since the binder quantity is constant between grades. In addition, the binder is batch processed with all of the fibers rather than adhered directly to individual fibers as with sizing, so it should present even less of an impediment to the electrolyte-fiber interface than sizing. The nonwoven samples are listed in order of increasing mat thickness. Cell failure and relatively poor performance were frequent for first three grades, possibly as a result of poor mat adhesion that creates stray fibers shorting the cell or becoming dislocated from the circuit. Chopped fiber nonwoven mats below a critical thickness of about 0.13 mm are therefore not recommended for future study. Of the remaining samples, capacity was found to generally improve with shorter fibers, possibly because the surface area increases. However, the best result is with the continuous fiber sample, which suggests that good fiber connectivity is at least as important as high surface area. Longer fibers also minimize the risk of dislocating stray fibers. COTS nonwoven mats are not as structural as woven fabrics, but they are easy to handle and the electrochemical performance is acceptable.

4. Conclusions

From these tests, the potential use of COTS materials as carbon anodes in power and energy storage applications is viable. Suitable de-sizing of the fibers did not show enough improvement over sized materials to require a de-sizing step, and all the materials were able to be tested as received. The PAN-based materials had the best overall electrochemical capacity and tensile properties and have the widest breadth of applicability for use in structural applications. The pitch-based fibers generally performed more poorly and would be best used only in applications where there is a strong need for other properties associated with pitch-based materials, such as high thermal conductivity. Considering both capacity and tensile strength, the difference in electrochemical-mechanical properties between many PAN-based fibers appears to be insignificant. A determination of the appropriate fiber for an application would depend primarily on the structural requirements, which enables the designing of a wide range of structural electrodes. The activated carbons, carbon nanotubes, and nanofoams demonstrated promise with both a good electrochemical capacity and high capacitance, although the fabric tensile strengths are too low for isolated use in structural materials.

In-depth analyses of the materials described here with regard to electrochemical-mechanical performance, cycling behavior, and morphology are underway and will be submitted to the peer-reviewed electrochemistry literature.

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Acronyms

AC	activated carbon
ARL	U.S. Army Research Laboratory
BPNT	bamboo multi-wall nanotube
CFF	fibrillated acrylic fiber pulp
COTS	commercial off-the-shelf
Da	dalton
FE-SEM	Field Emission Scanning Electron Microscope
LiPF ₆	lithium hexafluorophosphate
MWNT	multi-wall nanotube
PAN	poly(acrylonitrile)
PEO	poly(ethylene oxide)
SEI	solid electrolyte interface
SWNT	single-wall nanotube

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